Robust Nitrogen oxide/Ammonia Sensors for Vehicle on-board Emissions Control

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(NNSA Minority Serving Institutes Program)

Los Alamos National Laboratory
June 11th 2015

Project ID : ACE079

Los Alamos NATIONAL LABORATORY

Project Overview

Timeline

- Project Start Date
  - **October 2012**
- Project End Date
  - **September 2015**
- Percent Complete
  - **86%**

Budget

- Total project funding
  - 3 Years : \$1,050,000
  - DOE Cost : \$1,050,000
  - Cost Share : None
- Funding:
  Received in FY 15 \$ 350k
  For FY 16 \$ 0k

Barriers

NO_x sensors that meet stringent vehicle requirements are not available:

a) Cost (Complex sensors compared to the automotive λ sensor)

b) Sensitivity (Need ± 5ppm or better sensitivity)

c) Stability (Need ≈ 5000 hours)

d) Interference (P_{O2}, P_{H2O}, hydrocarbons)

e) Response time (< 1 sec)

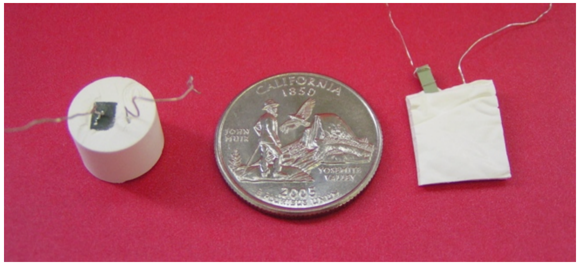
Partners

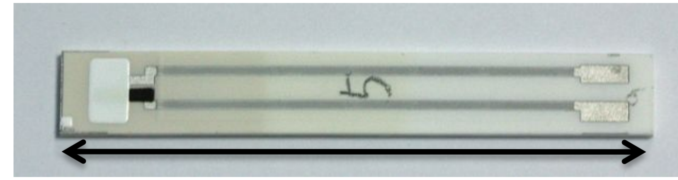
- LANL – Project Lead, Design, Testing
- ESL ElectroScience – Sensor prototype manufacturer
- Custom Sensor Solutions, Inc – Sensor electronics developer
- Washington State University – Pulse Discharge Technique
- ORNL - National Transportation Research Center. No cost. Funded directly by VT
- Rutgers University (no cost) –Signal processing
- Zircoa Corporation (NDA/MTA)

Relevance

- From VT Program MYPP 2011-2015
  - Table 2.3-3 Tasks for Combustion and Emission Control R&D
  - Task 3. *Engine Technologies R&D (fuel systems, sensors and controls, integrated systems, etc.)*
    - Develop and validate NO_X and PM sensors for engine and after-treatment control and diagnostics
    - GOAL: By 2013, develop NO_x sensor materials and prototypic NO_x sensors that meet the sensitivity requirements identified by industry for emissions control in light duty diesel engines.
- Objective of the project is to develop low cost robust nitrogen oxide/ammonia sensors
- Accurate fast and reliable sensors can:
  - Improve efficiency of emissions system
  - Verification of emissions–system efficiency
  - Help validate models for the degradation of exhaust after treatment system
  - Potential feedback for effective engine control

Approach (Previous Project)

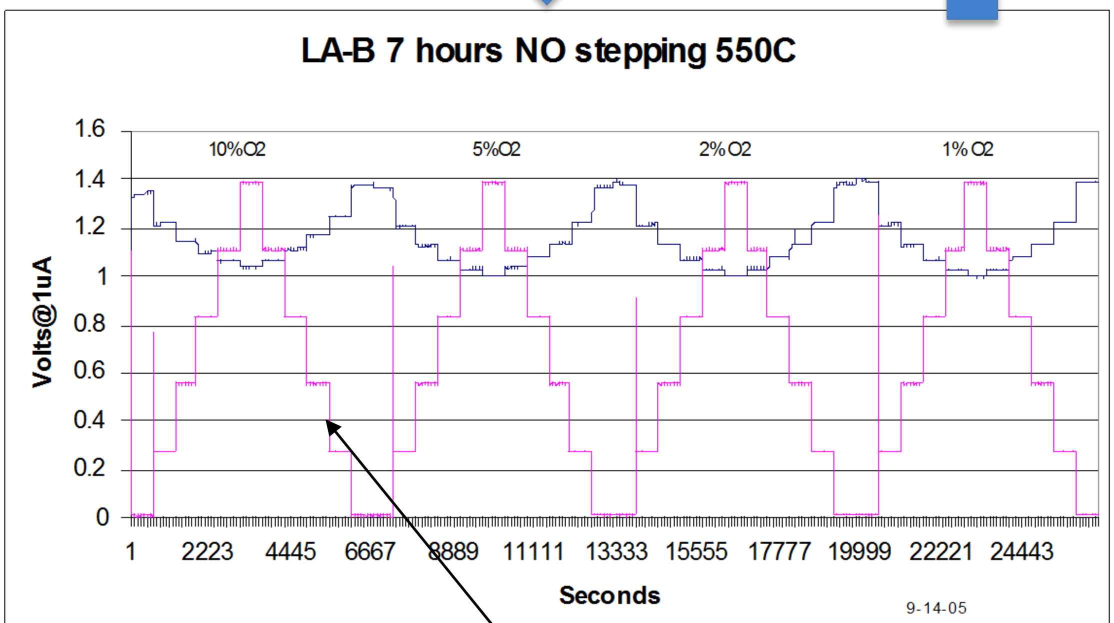




50 mm

Excellent performance of bulk sensor achieved

Need to retain performance in a commercially manufacturable device, validate, and transfer technology to industry

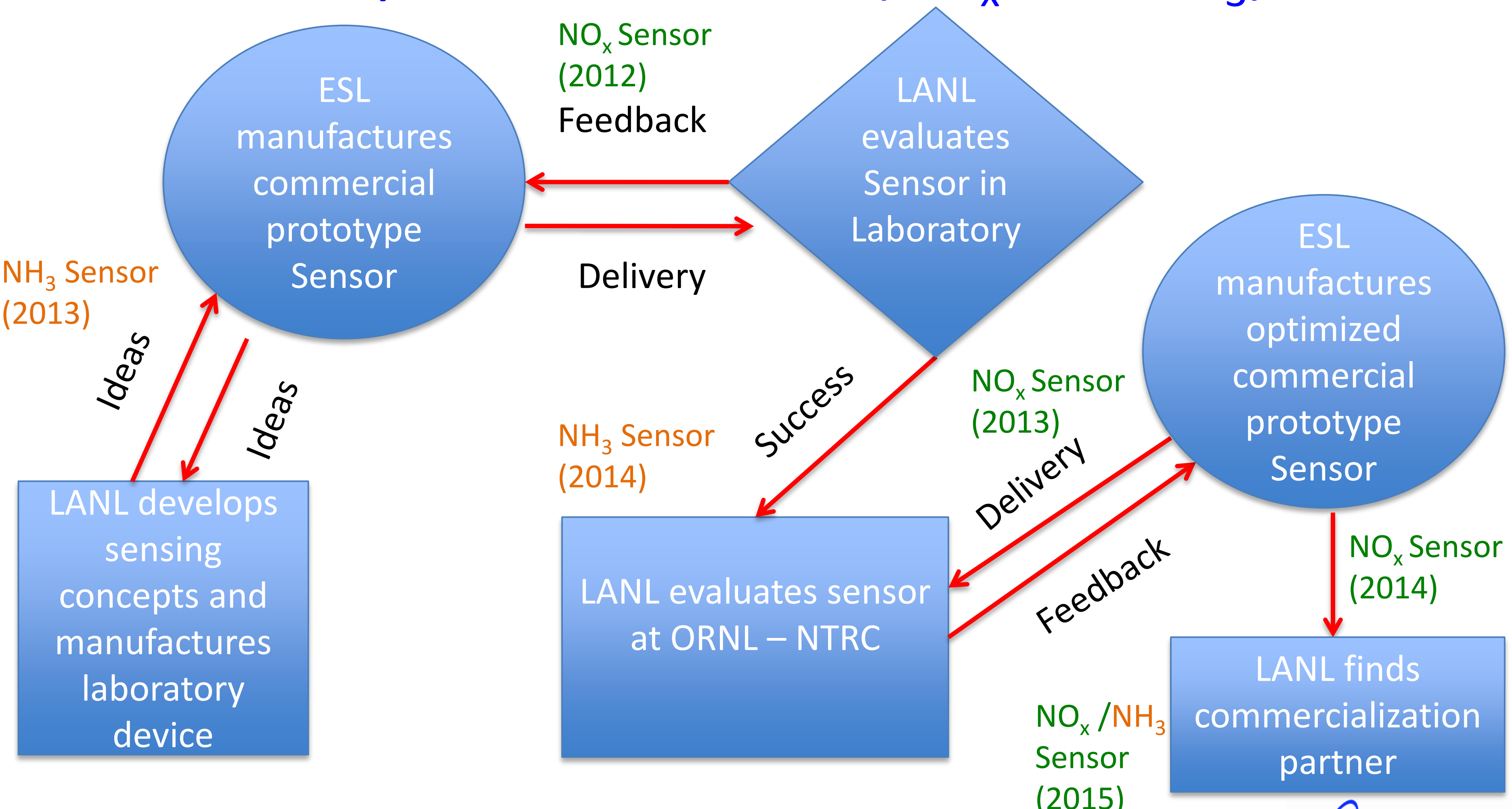


NO Mass flow controller

Data obtained by FORD Motor Co.
R. Novak, R. Soltis, D. Kubinski, E. Murray and J. Visser
September 2005

Approach

- Solve key issues impeding commercialization of mixed potential sensors (NO_x and NH_3)



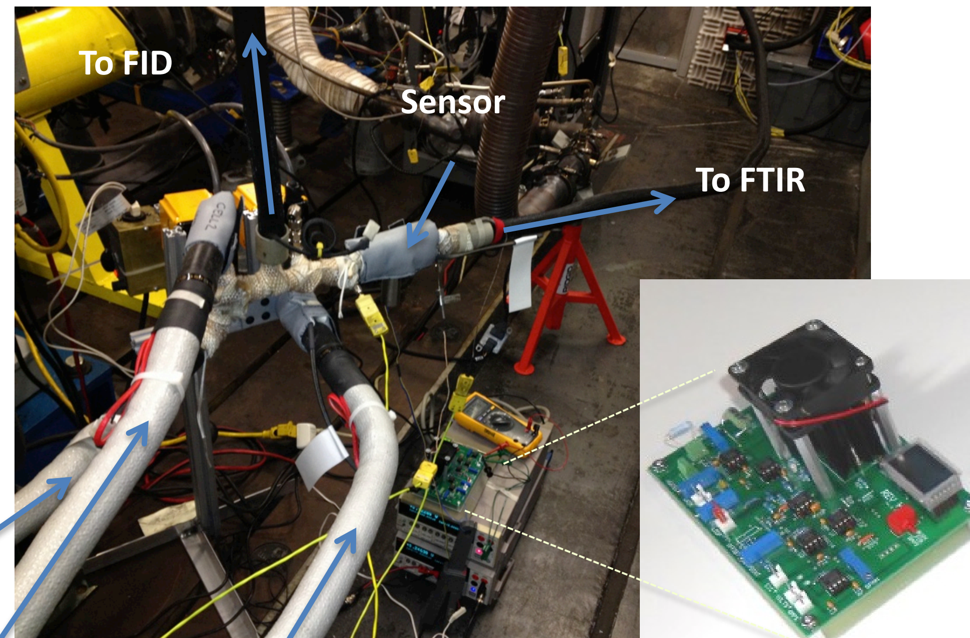
Approach - Milestones

- Milestone 1 (Dec 2014): Demonstrate NH_3 sensor response in an engine equipped with a simulated SCR system. (Complete)
- Milestone 2 (March 2015): Complete evaluation of Sulfur tolerance of NO_x sensor. (Complete)
- Milestone 3 (June 2015): Complete 3-electrode button cell studies on thee different perovskite electrode compositions. (Initiated: On track)
- Milestone 4 (Sept 2015): Demonstrate improved sensor selectivity by use of a catalytic layer on the overcoat of a NO_x sensor. (Initiated: On track)

NO_x/HC Sensor - Engine Evaluations

2014 AMR

- ✓ **1st Campaign**: March 2013.
  - Primary focus, evaluati NO_x response, sensor control electronics, data acquisition system, and sensor packaging
- ✓ **2nd Campaign**: January 2014.
  - Sensor in gas stream (flow restrictor removed)
  - Repeat NO_x, EGR experiments from Round 1 with improved sensor packaging
    - Stainless steel cap / internal shield
  - Perform cold-start experiments
    - Capture NO_x (post-DOC) and HC (post-DOC and engine out) data sampling configurations
  - Acquire data from sensor power supplies to understand behavior of sensor control systems
    - Heater voltage with simultaneous measurement of heater current to provide real-time data on sensor heater resistance and therefore sensor temperature
  - Perform EGR sweep experiments in NO_x and HC modes



Engine out

GM 1.9L CIDI Engine

DOC out

$HC/NO_x/NH_3$ Sensor - Engine Evaluations

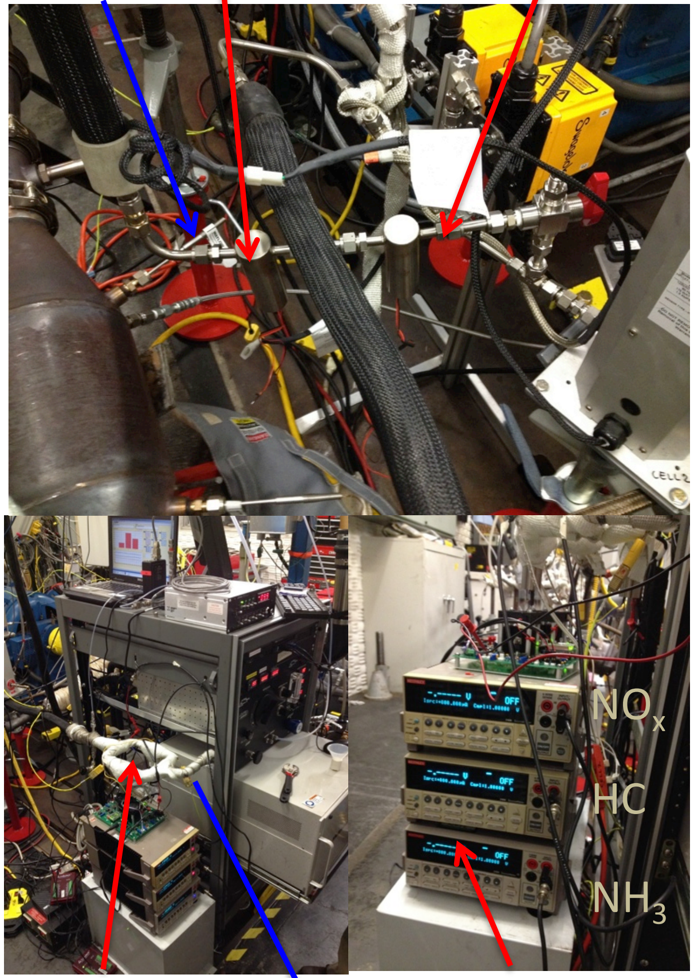
Technical Accomplishments

✓ **3rd Campaign**: March 2015.
  - Simultaneous evaluation of NO_x, HC, and NH_3 sensors w/o attempting to repeat dyno runs.
  - Added 4th (HC) to measure impedance of YSZ electrolyte to measure how well heater resistance feedback and power supplies fix operating T.

- Start-up : collected HC, NO_x, and NH_3 data before and after TWC.
- Vary engine load when operating in lean homogeneous and lean stratified operation.
- Lambda sweeps ($0.98<\lambda<1.8$) to determine characteristics of individual sensors over large changes in background PO_2.
- Inject known concentrations of NH_3 from bottle post TWC and upstream of NH_3 and NO_x sensors during lean operation (PO_2>5%) to simulate slip events from SCR.

BMW 120i GDI Engine

FID HC sensor #2 HC sensor #1



NO_x & NH_3 sensors in parallel

FTIR

Keithley 2400 sensor voltages

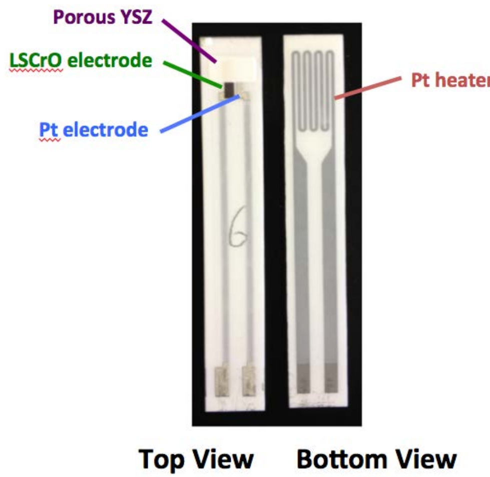
HC, NO_x and NH_3 Sensors

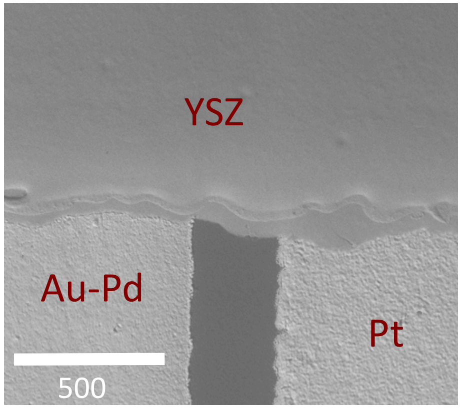
Technical Accomplishments

HC Sensor: Pt//YSZ//LSCO
Operation @ 0 bias

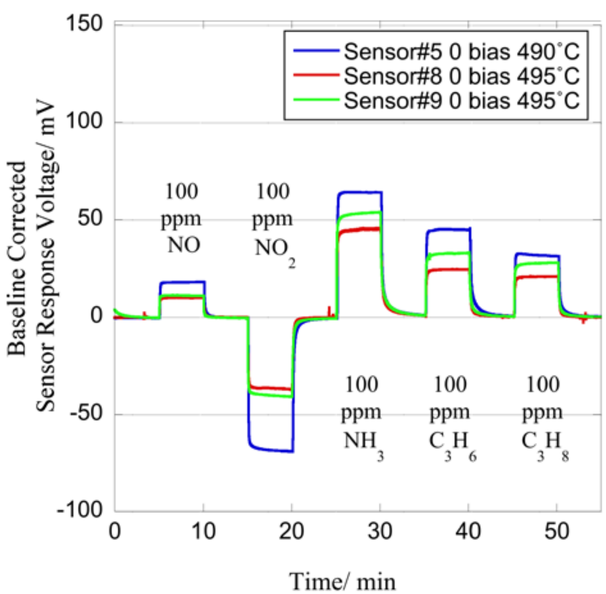
NO_x Sensor: Pt//YSZ//LSCO
Operation @ +ve current bias

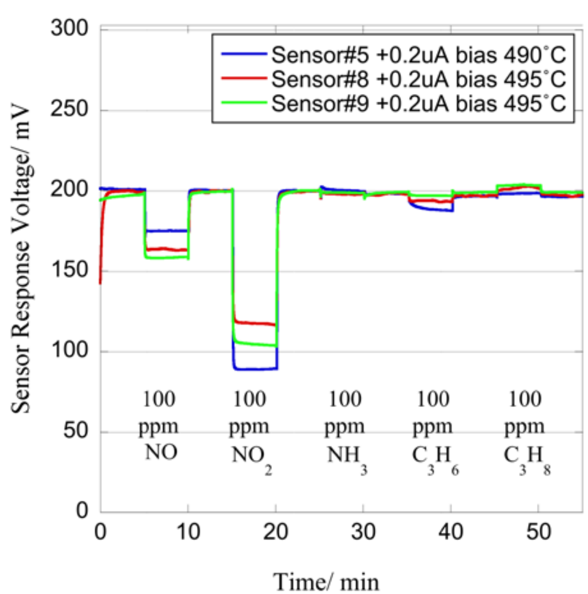
NH_3 Sensor: Pt//YSZ//Au
Operation @ 0 bias

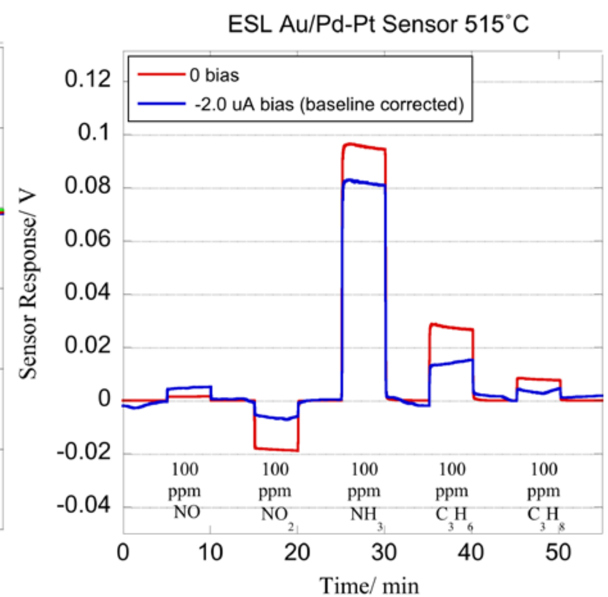




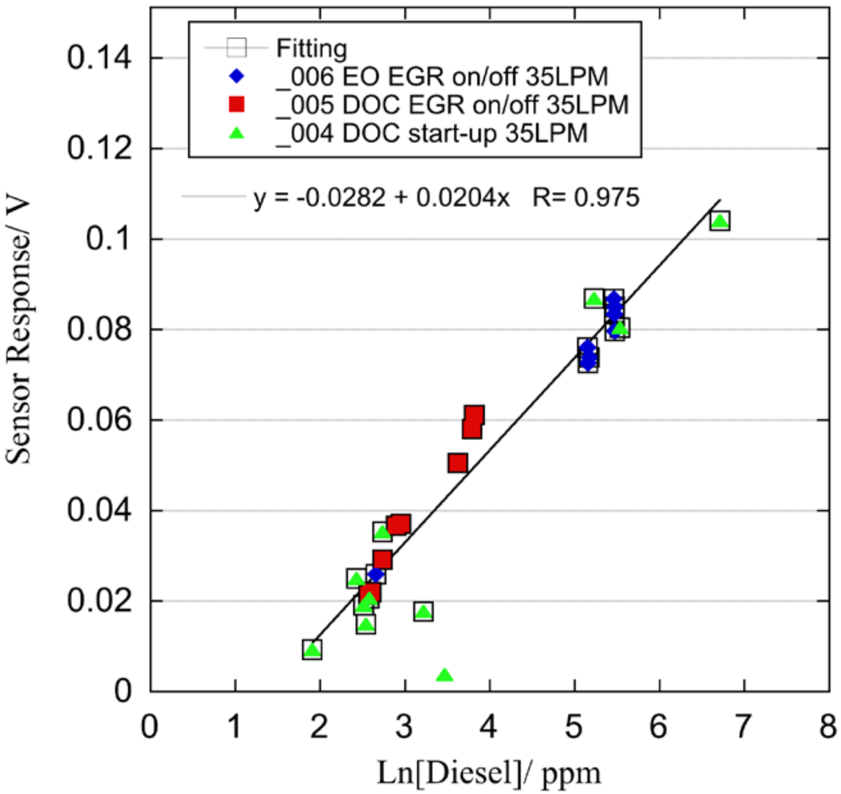
Potential to combine all 3 on one stick sensor

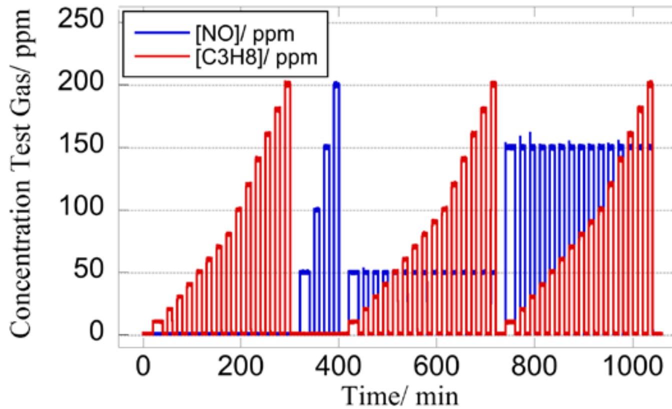


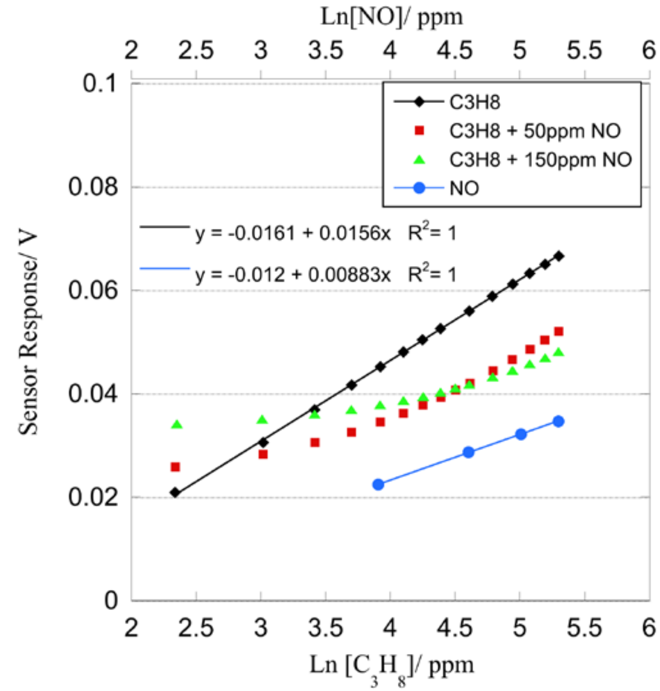




HC Sensor – Calibration



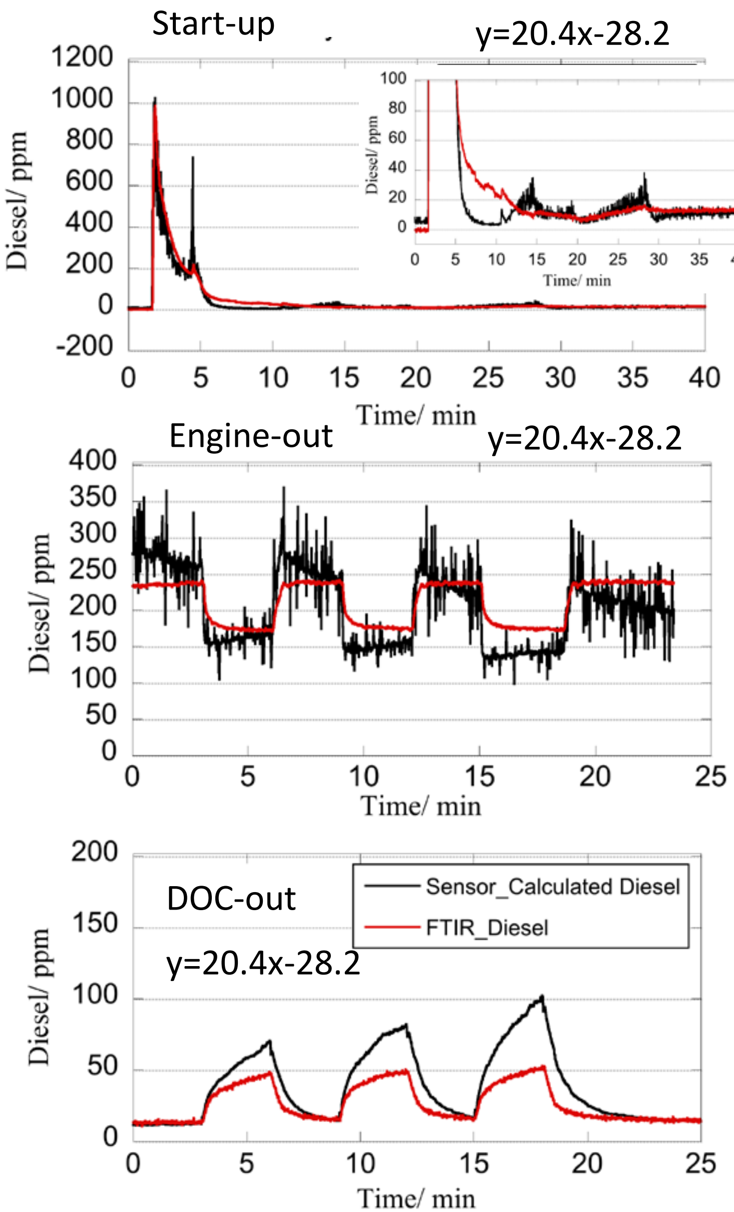




- ✓ Sensor quantitatively tracks total HC concentration
- ✓ Higher slope obtained in engine evaluations than lab calibration
  - Sensor responding to higher order hydrocarbons
    - (tracks total carbon in exhaust gas)

HC Sensor Performance

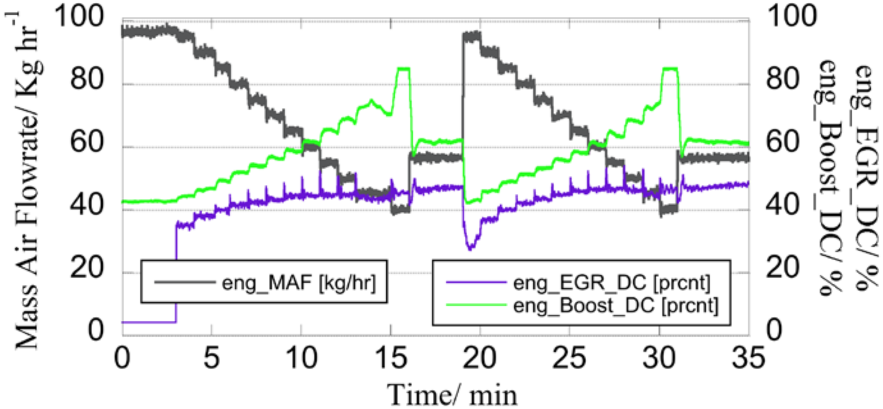
Technical Accomplishments

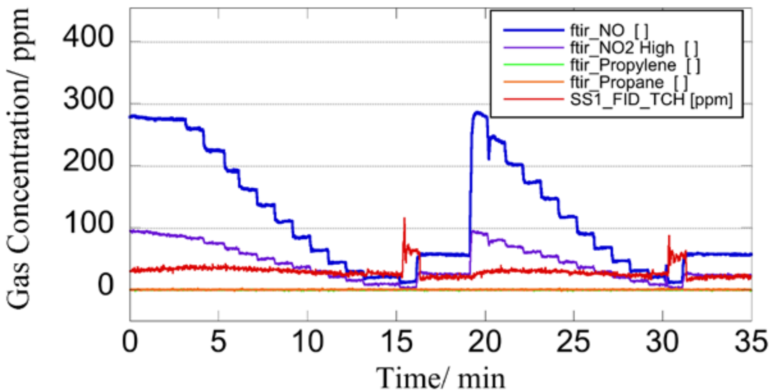


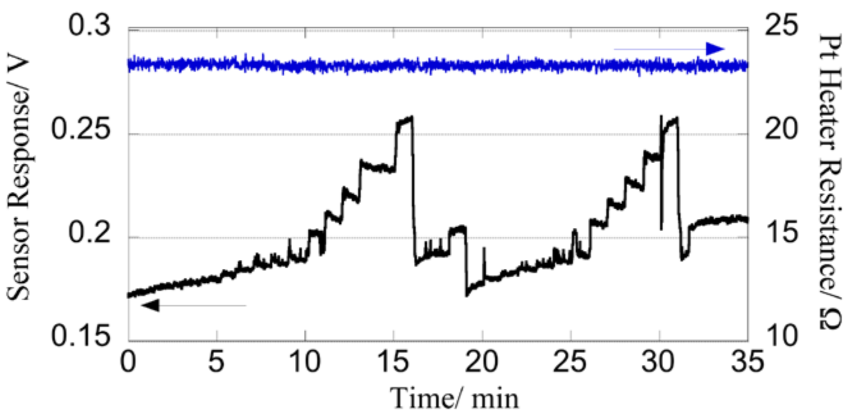
- Transients in HC content tracked by sensor voltage response.
- When sensor is sampling Engine-out exhaust, response is noisy. Calculated Diesel concentration from sensor response ±40ppm FTIR measurement.
- DOC out sensor signal less noisy, but sensor over predicts Diesel content by as much 50ppm compared to FTIR measurement.

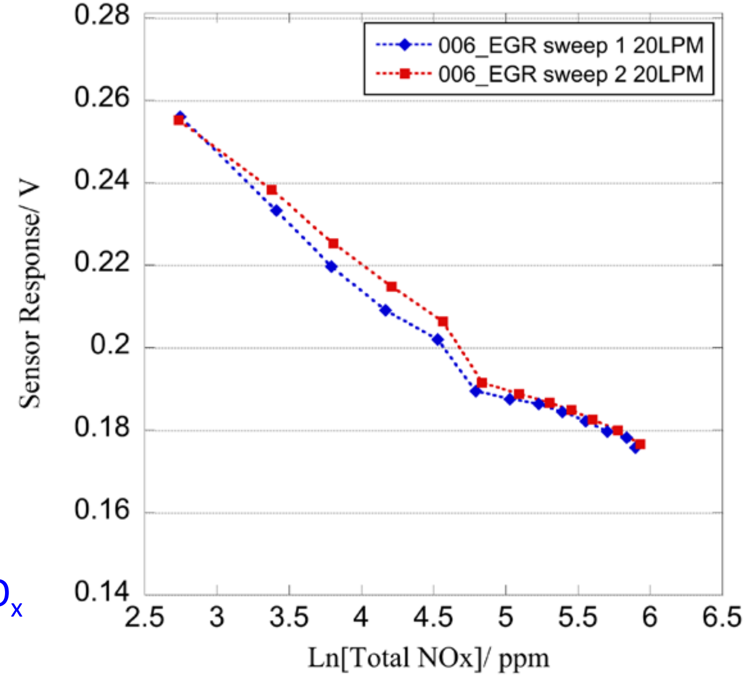
- Issues to be resolved
  - Change in HC speciation as exhaust gas transports to instruments?
  - Non- trivial influence of interferent species?

NO$_x$ Sensor – Step EGR

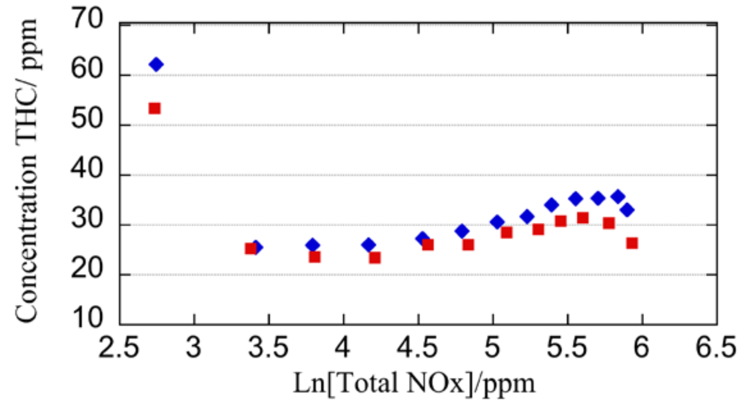




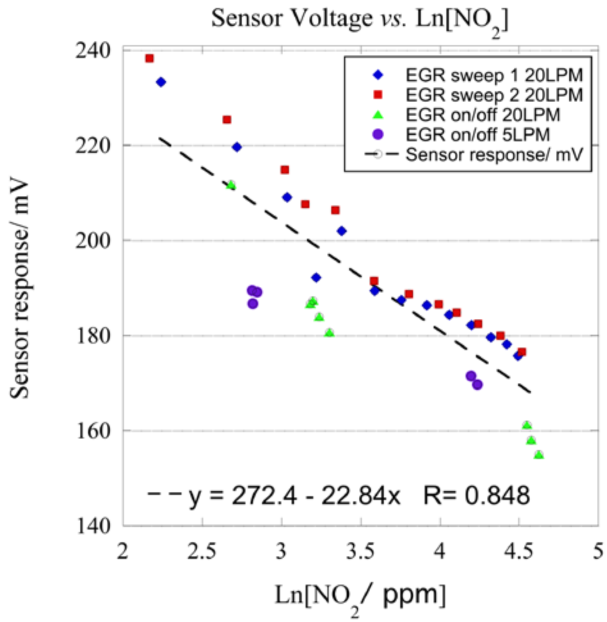


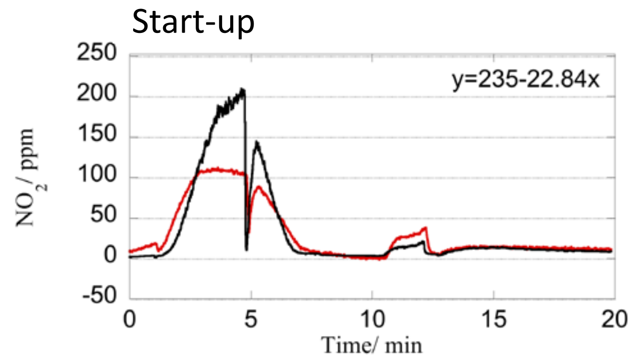


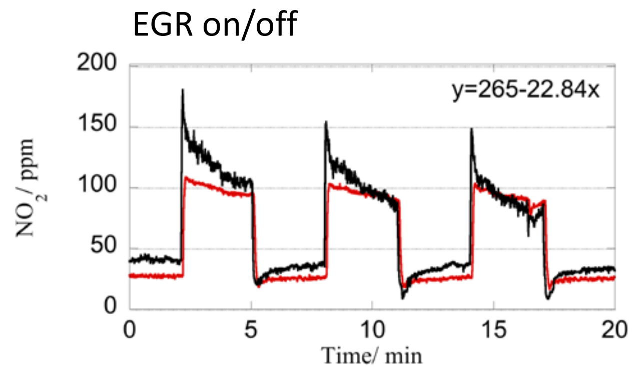
- ✓ Sensor quantitatively tracks total NO$_x$ concentration

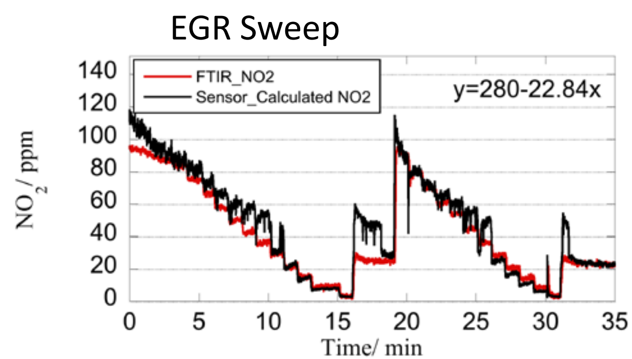


NO_x Sensor performance (CIDI)









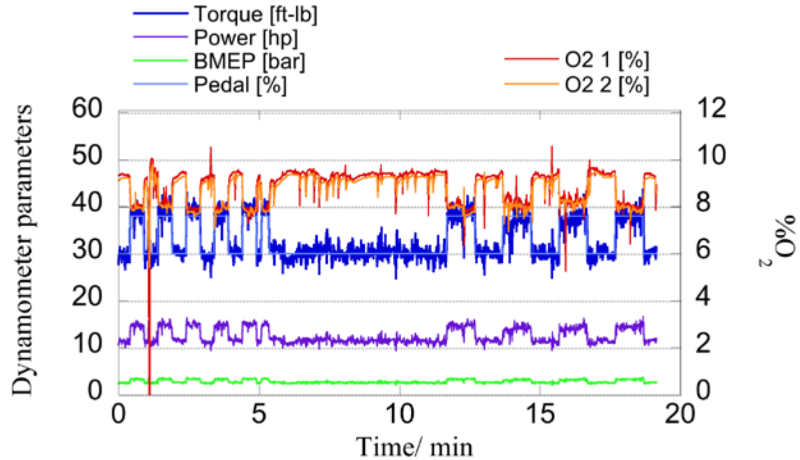
- Calibration curve used for comparing sensor voltage response to concentration of NO_2 only.
- Sensor voltage response during start-up appears to primarily track NO_2.
- For EGR on/off and sweep experiments, concentration calculated sensor response voltage is equally comparable to both $NO+NO_2$ and NO_2 only (when using the respective calibration curves).
- *Y*-intercept likely correlated to [THC] or other interferents but not in trivial (linear) way.

NO_x Sensor performance (GDI)

Technical Accomplishments

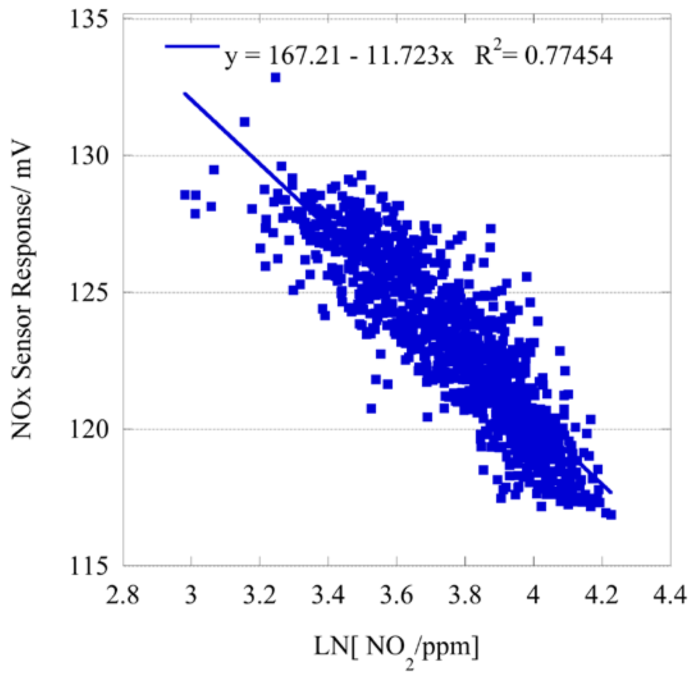
First test of NO_x sensor with overcoat in dynamometer

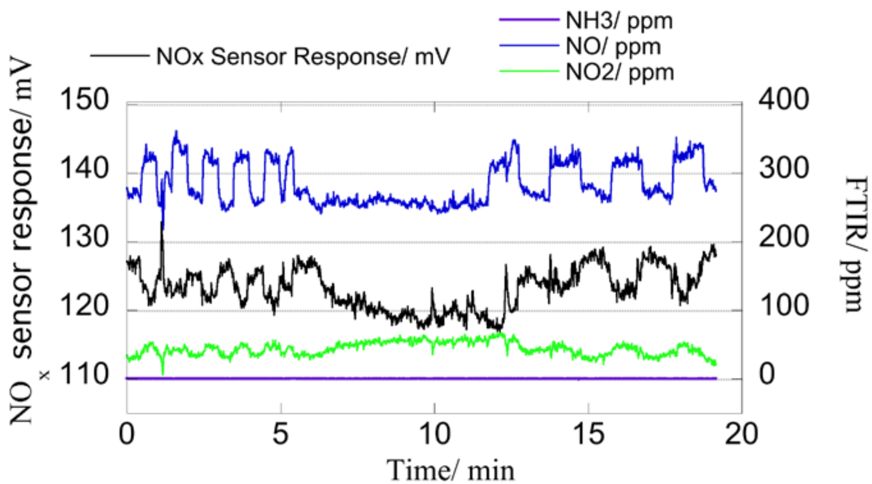
- Sensor tracks NO_2 concentration from FTIR
  - Good fit over all NO_2 concentrations
  - Insensitive to varying P_{O2}, P_{H2O} and hydrocarbons
- Improved sensitivity/selectivity can result in tighter calibration



λ: 1.86-1.62

Vary load

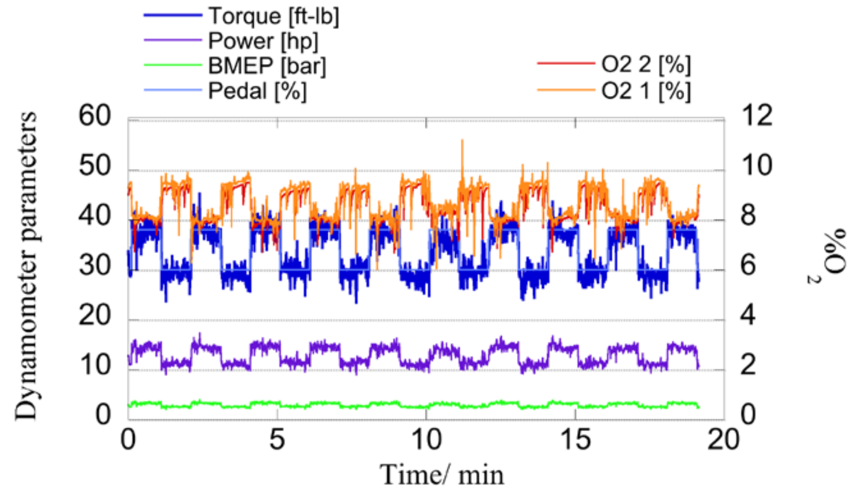




NH_3 sensor response

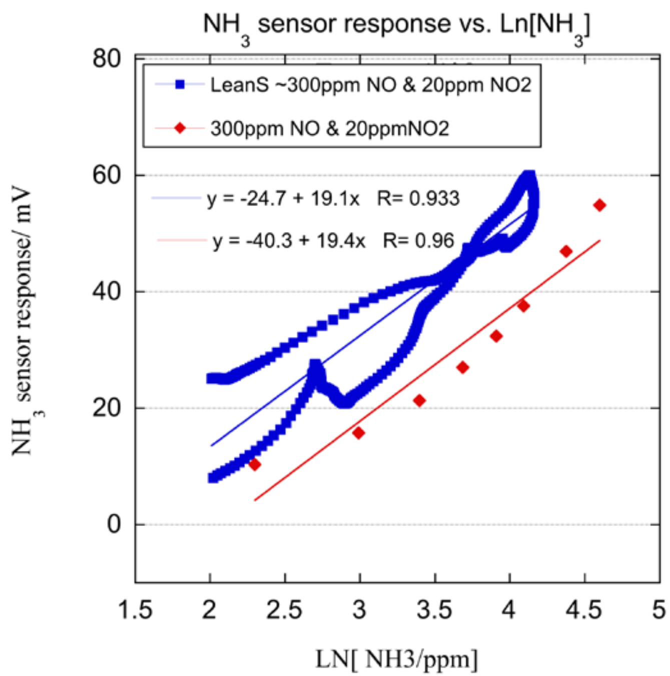
NH_3 sensor successfully tested in dynamometer for first time

- Sensor tracks NH_3 injected after 3-way catalyst
  - Calibration under dry gases in lab over estimates concentration
  - Further tests underway to obtain appropriate calibration curve



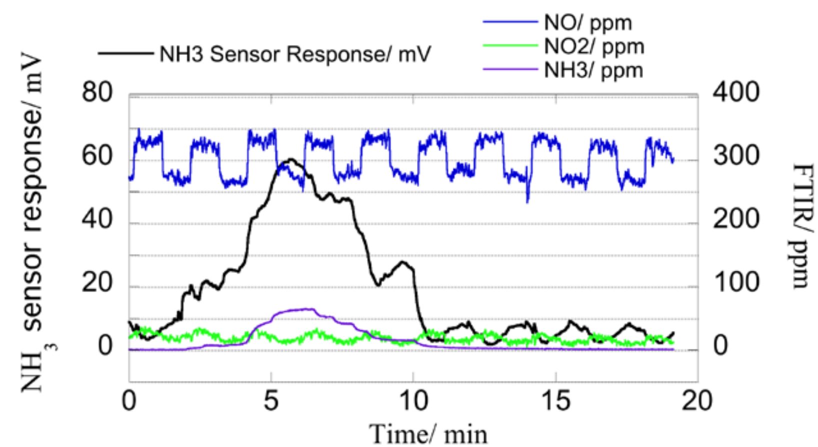
Engine in lean-stratified mode, vary load

Inject NH_3 into exhaust stream post TWC



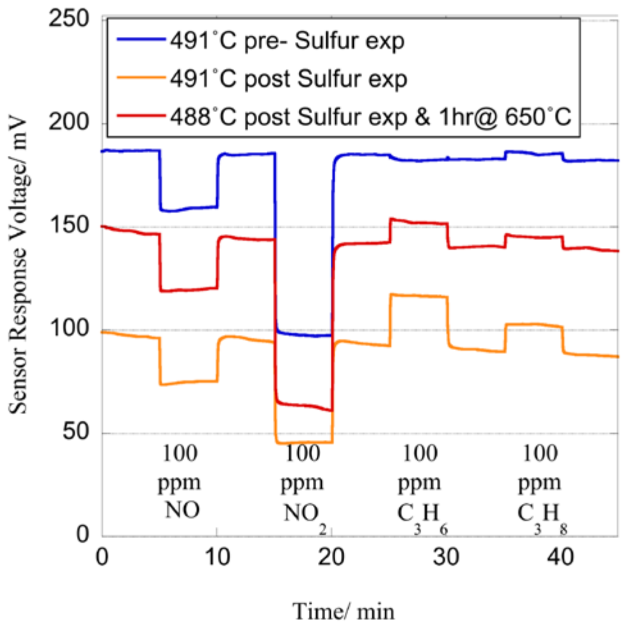
Compare Dyno data with lab calibration

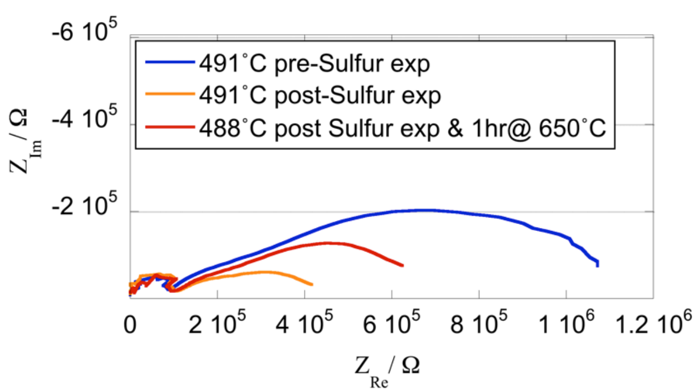
MILESTONE 1



Sensor Tolerance to Impurities

Technical Accomplishments





Engineering Specification (ES)

- Sensor response to 100 ppm each NO, NO_2, C_3H_6 and C_3H_8 in 10%O_2, 10%H_2O, balance N_2 measured before and after sulfur exposure
- Impurities testing conditions:
  - Sensor held at 500˚C
  - 50 hour exposure to:
    100ppm H_2S
    1000 ppm SO_2
    10%H_2O
    10% CO_2
    balance N_2

No O_2 present during this test. Sensor not designed to operate under rich conditions for extended periods of time

- Sensor response measured immediately after sulfur exposure was suppressed relative to initial response
- After "clean-up" heat treatment, sensor response approached initial, pre-exposure response.
- Shorter heat treatment at higher temperature likely to recover initial sensor response.

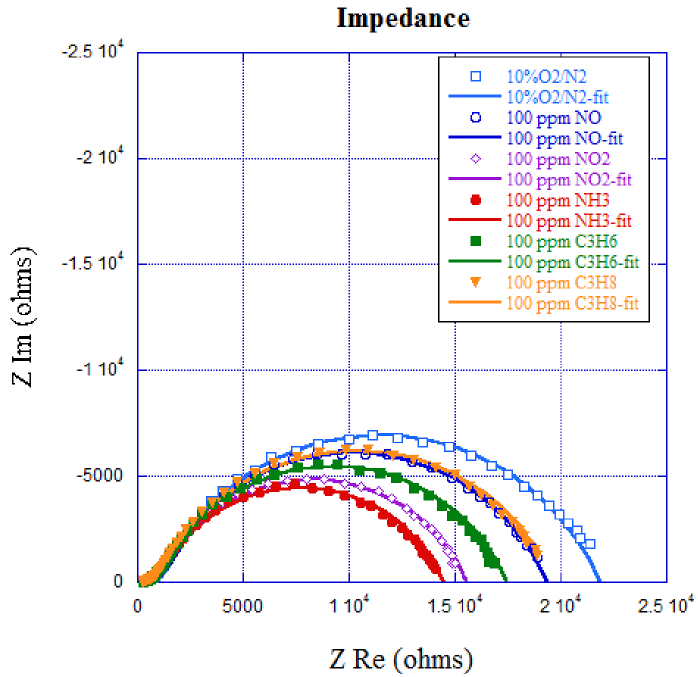
MILESTONE 2

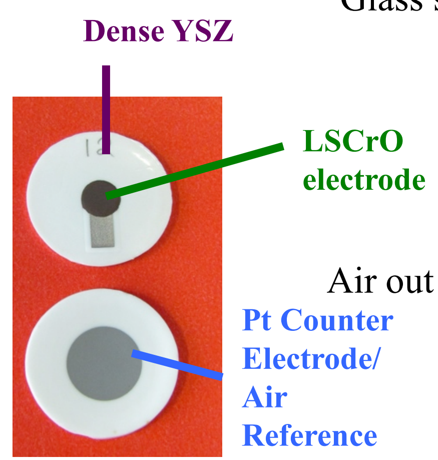
Improve Sensitivity/Selectivity

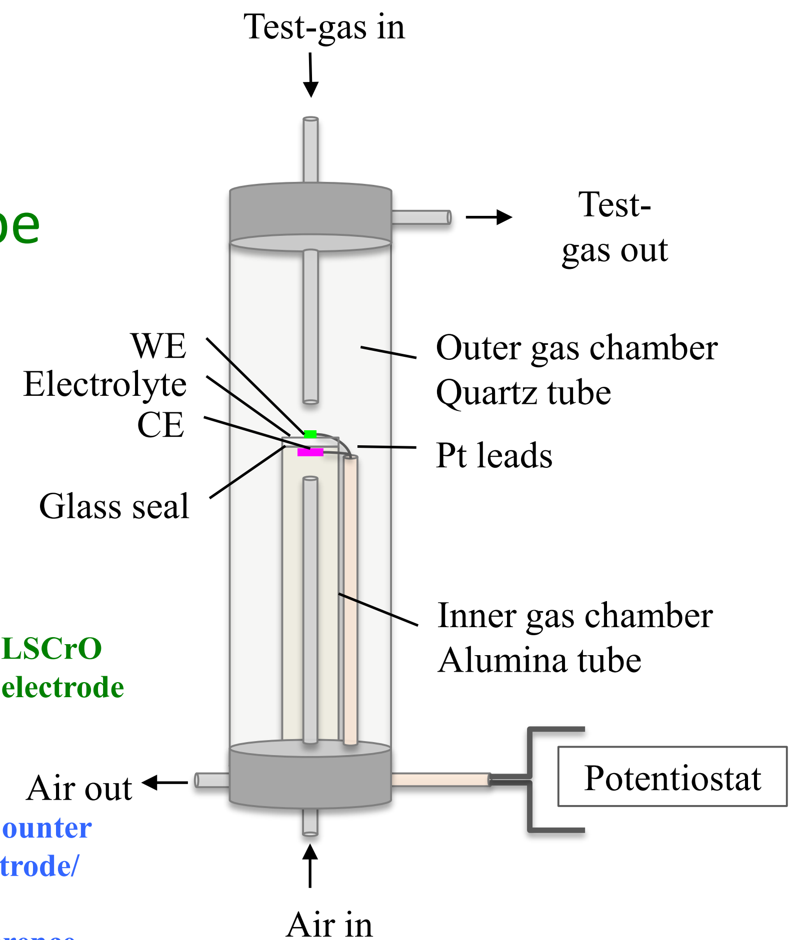
Technical Accomplishments

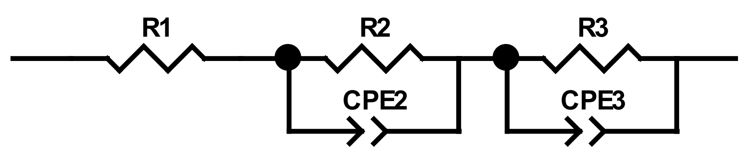
- Electrode optimization
  - Utilize 3-electrode setup
  - Extensive Impedance Spectroscope

Optimized compositions to be incorporated into stick sensor









MILESTONE 3

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Improve Selectivity

- Incorporate catalyst on top of protective overcoat
  - Catalyst has potential to optimize selectivity
- Preliminary results indicate that catalyst needs optimization

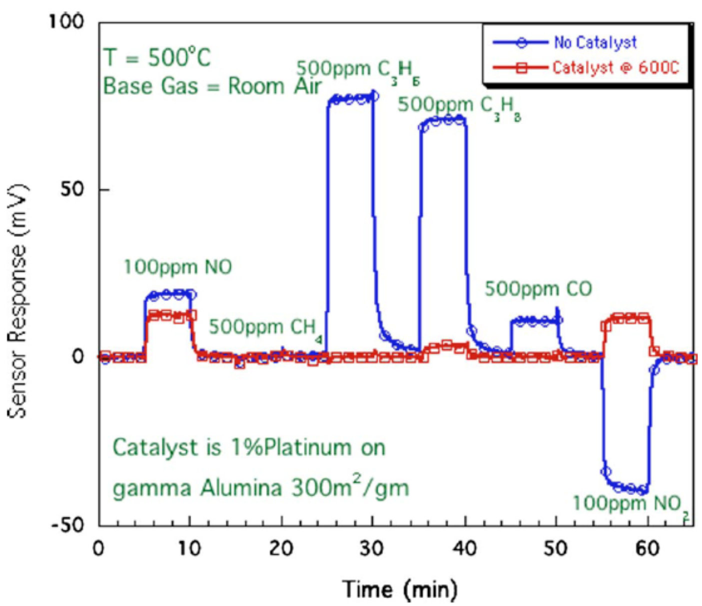
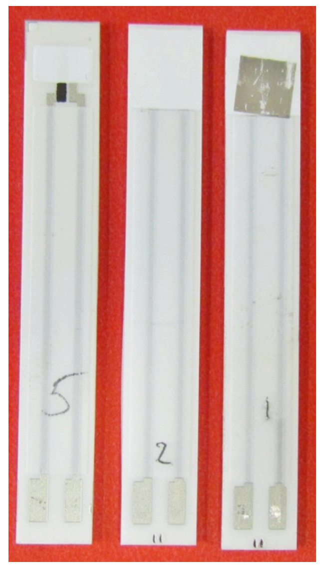
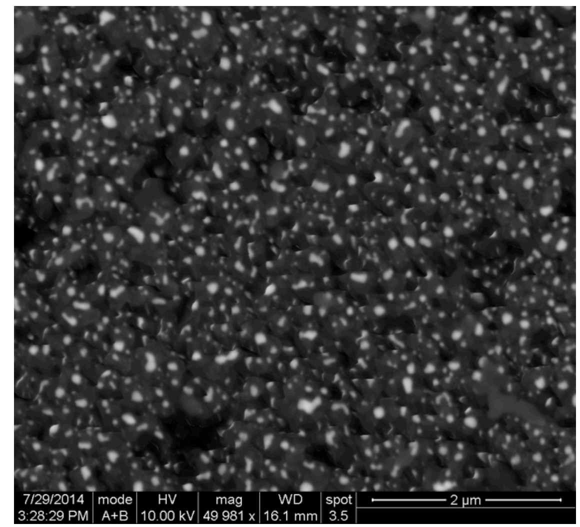


Figure 1. (Color online) Selectivity of a Pt/YSZ/$La_{0.8}Sr_{0.2}CrO_3$ sensor with and without a Pt/γ-Al_2O_3 catalyst.

Electrochemical and Solid-State Letters, **10** (2) J26-J29 (2007)
1099-0062/2006/10(2)/J26/4/$20.00 © The Electrochemical Society



Left to Right: Non-Overcoat, Overcoat, Pt Catalyst.



SEM image showing isolated Pt- particles (white) on top of porous alumina overcoat (black)

MILESTONE 4

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Commercialization Efforts

Technical Accomplishments

- NDA/MTA being negotiated with Continental, Ford, Chrysler and SWRI® to ship sensor systems for evaluation. Provided information to Delphi.
- LANL issued a broad Call for Commercialization Partners (RFI/RFP)
  - Released on 11/7/14 to 45 companies; Call closed on 12/8/14
  - Received 5 Letters of Interest from a variety of OEMs, Tier 1 suppliers and sensor development companies
- LANL Webinar
  - Successful interaction with 5 potential commercialization partners on Jan 28th, 2015
  - Presentations shared with all the participants
  - 1 company expressed interest in further evaluating sensors at their test facility under NDA/MTA
  - Several companies submitted "Product Commercialization Plans" by the Feb 25th deadline
  - LANL selected one company and is currently negotiating a license and potential CRADA for additional collaborative development to accelerate time to market.
- Commercialization of promising technologies takes time:
  - *The real need for a low cost robust NO_x sensor technology presents ideal timing for a successful Lab-Industry partnership*
  - *Packaging may involve further sensor modifications/development.*
  - *Further improvements in sensitivity and selectivity would increase the probability of successful commercial deployment of this technology. Calibration under dynamometer conditions needs to be more robust.*

Responses to Previous Year Reviewers' Comments

- The development of low cost, robust, and accurate NO/NH_3 sensors would help improve efficiency and lower emissions. The reviewer commented that it would help validate models for the degradation of exhaust after treatment system, and would help develop better engine controls. The reviewer said that sensors are currently expensive. This person further noted only one supplier of NO_x sensors and possibly two suppliers of NH_3 sensors, and noted that these sensors are critical to high-efficiency closed loop control and OBD.
  – This project has developed the technology to a level where Tier I suppliers/OEMs are interested. In the future, expand the use of these sensors to model validation and develop better engine controls in collaboration with ORNL.
- The reviewer commended that the project had made very good progress. However, according to the reviewer engine results are troubling. The scatter is 150 to 400 ppm diesel at approximately 80mv response. The best plots are response to concentration. Time plots are only useful for time response, not for concentration response.
  – Have used various calibrations to provide quantitative comparison of sensor response and gas concentration in engine dynamometer. The future work is geared to improving the sensor sensitivity/selectivity by optimizing electrode composition and incorporating heterogeneous catalysts.
- The reviewer found that the project appeared to have engaged university, national laboratory, and industry partners effectively and was commended for actively seeking commercialization paths for this innovative technology. The reviewer suggested that a real sensor manufacturer needed to be recruited. The reviewer suggested that next must be OEM or Tier 1 automotive manufacturer input to confirm requirements and critique of implementation to significantly improve the product development speed and final result. The reviewer observed good initial work to get stable linear output, and, as mentioned above, improving the full range signal would likely require on-sensor electronics development and continued engine testing for sensor stability. The reviewer concluded that the current budget did not appear to comprehend these activities in whole. The reviewer recommended an OEM/Tier 1 partner for additional funding.
  – Commercialization activities were initiated this FY and a Tier 1 supplier has been identified as a partner to further the development of these sensors. LANL will address improving sensor sensitivity/selectivity and work closely with sensor manufacturers to develop packaging.

Collaboration

Eric Brosha, Cortney Kreller, Roger Lujan, and Rangachary Mukundan
Students: Shanice Brown and Jonathan Reynolds
Fundamental mixed potential sensor R&D
Sensor design, materials selection, laboratory testing

Ponnusamy Palanisamy
Manufacturing, scale-up, valuable feed back in sensor design

Bill Penrose
Custom sensor control electronics: Heater control and High impedance boards

National Transportation Research Center
Vitaly Y. Prikhodko, Josh A. Pihl, and James E. Parks II
Sensor test site.
No Cost Partner
Directly funded by VT

Washington State University (Praveen Sekhar)
Zircoa (Boris Farber)
Utilizing PDT to improve sensor selectivity

Rutgers University (No cost)
(Alexandre Morozov)
Utilizing Bayesian methods to improve sensor selectivity

Licensing agreement with a Tier 1 supplier is under negotiation

Future Work

- Optimize sensors
  - Improve sensitivity/selectivity by selection of appropriate electrode compositions
  - Improve selectivity by use of catalyst coating over sensor protective overcoat
- Work with Commercialization partner
  - Tier 1 supplier will lead commercialization efforts (Licensing agreement under negotiation)
  - ESL will work closely with Tier 1 supplier to transfer processing details
  - LANL will work closely with Tier 1 supplier to successfully transfer technology
    - Electronics package development
    - Extensive dyno evaluation
- Expand sensors to support EERE emission control research and development (collaboration with ORNL)
  - Provide inline (non-extractive) NO_x, HC, NH_3 sensing capability
    - Better evaluate engine control technology
    - Model validation

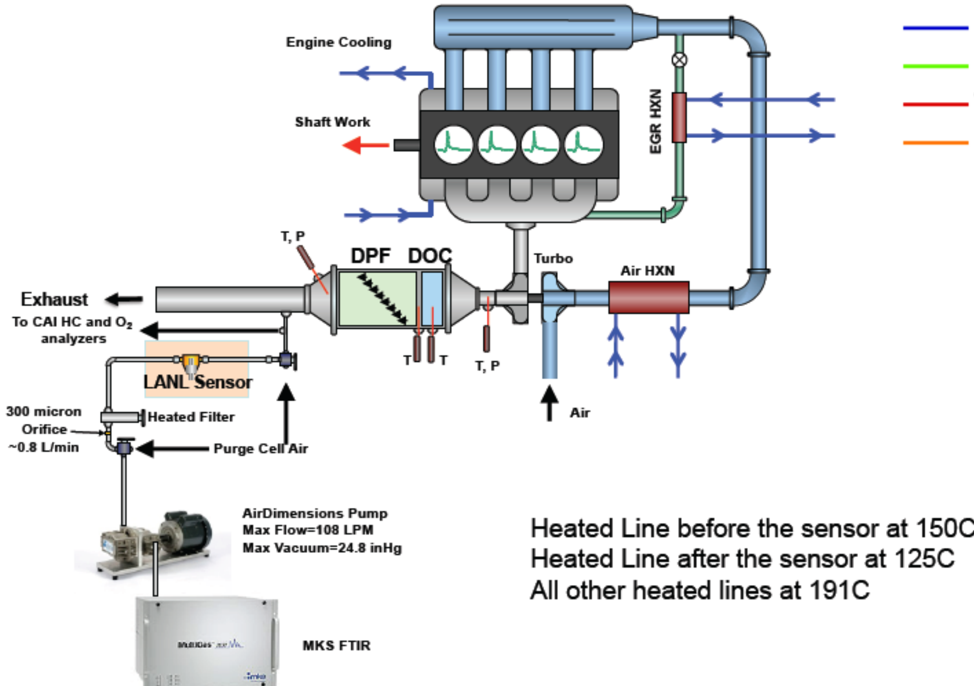
Summary

- Successfully transformed LANL patented mixed-potential sensor technology to a commercial manufacturing platform
  - HTCC process (ESL collaboration)
- Demonstrated capability of HC, NO_x and NH_3 sensors during engine dynamometer evaluations at ORNL – NTRC
  - 1st campaign: qualitatively evaluate sensors and identify problems
  - 2nd campaign: quantify NO_x and HC sensors in CIDI engine
  - 3rd campaign: simultaneously quantify NO_x, HC and NH_3 sensors in GDI engine
- Identified commercialization partner (Tier 1 supplier)
  - Licensing under negotiation
  - Will work closely with Tier 1 supplier and ESL to commercialize technology
- Improve sensor sensitivity and selectivity to facilitate calibration and signal processing
- Integrate sensors with dynamometer to provide gas composition data at various locations (non-extractive)

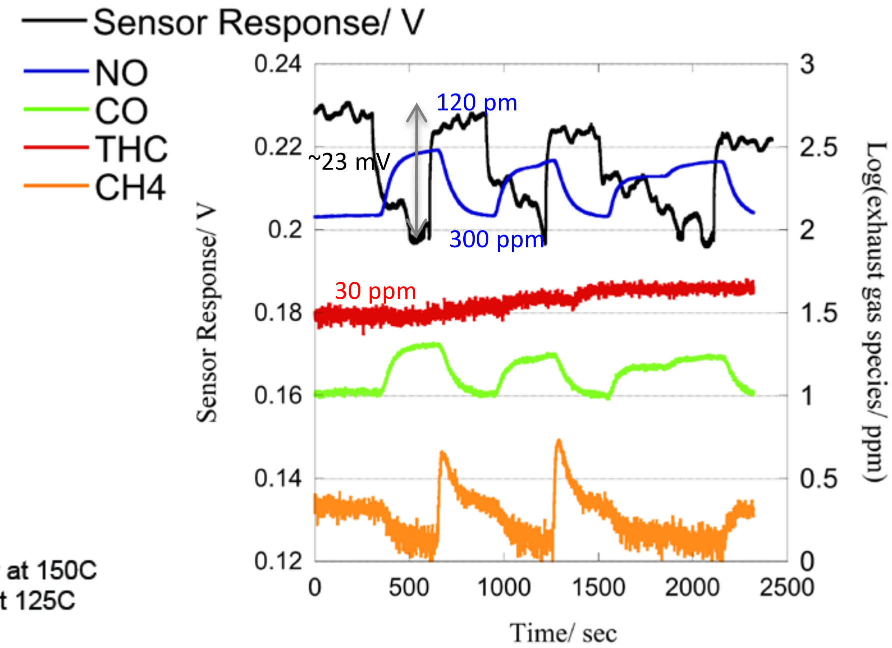
Technical Back-Up Slides

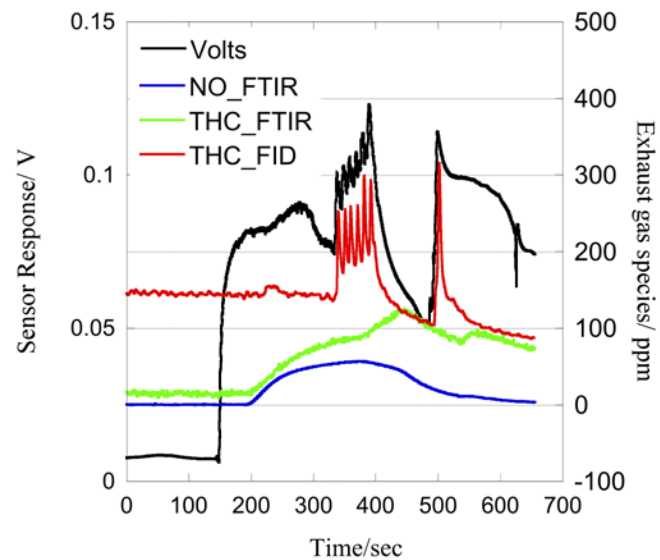
NO_x Sensor - Engine Evaluations

2013 AMR



LANL HC & NOx Sensor
Engine Setup at ORNL, March 2013



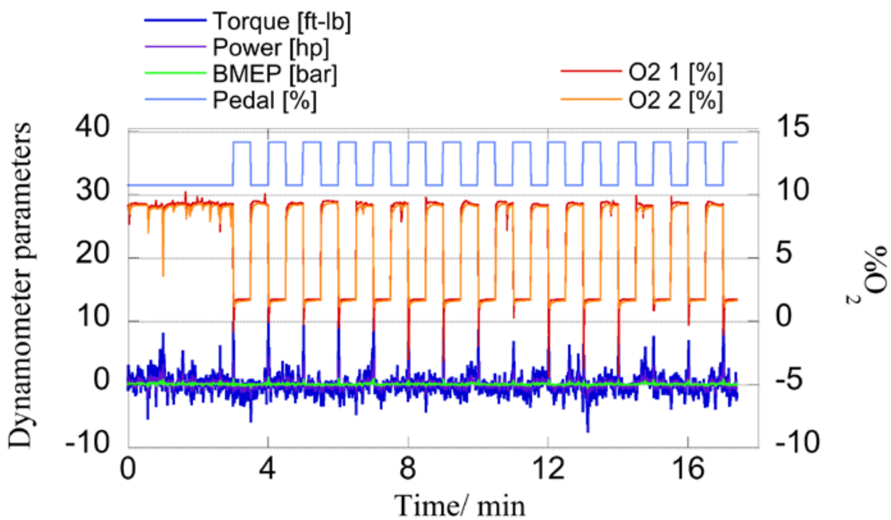


- Test LANL sensors under realistic conditions
- Validate response with analysis equipment
- Identify potential issues with sensor
- Provide feedback to develop better sensors

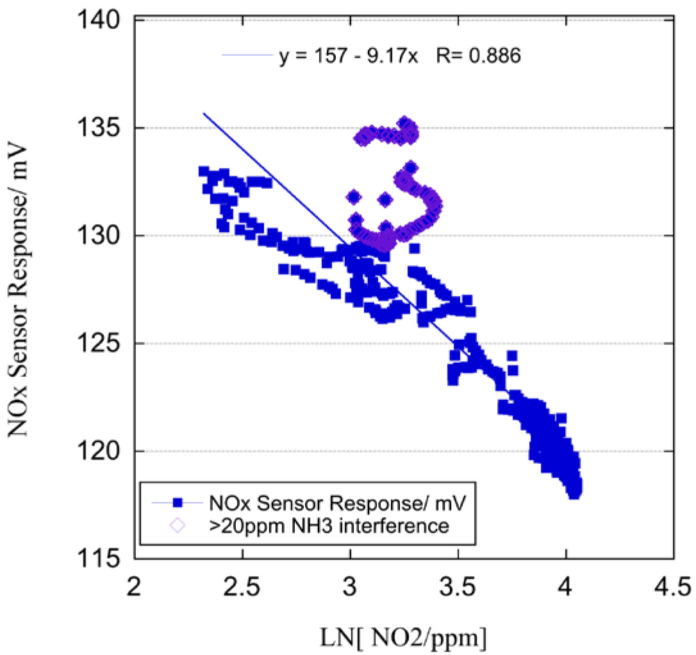
Engine Evaluations: NO_x sensor response

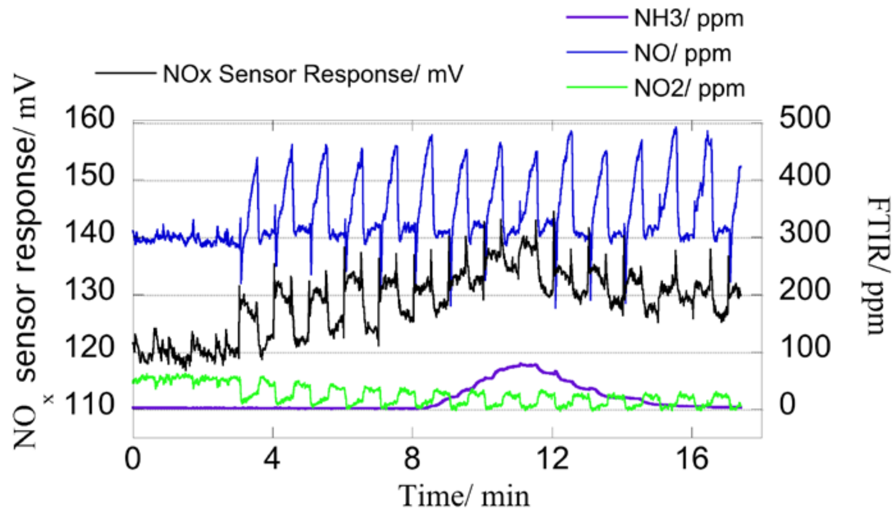
Technical Accomplishments

- Sensor tracks NO_2 concentration from FTIR
  - Good fit over all NO_2 concentrations
  - Insensitive to varying P_{O2}, P_{H2O} and hydrocarbons
  - Interference from >20ppm NH_3



λ switching 1.1 → 1.8





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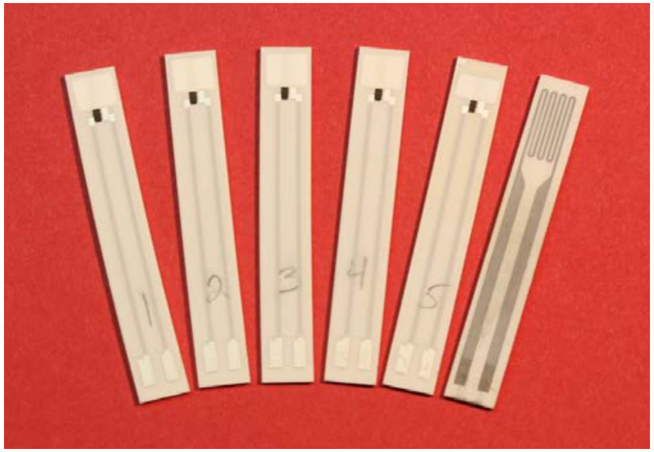
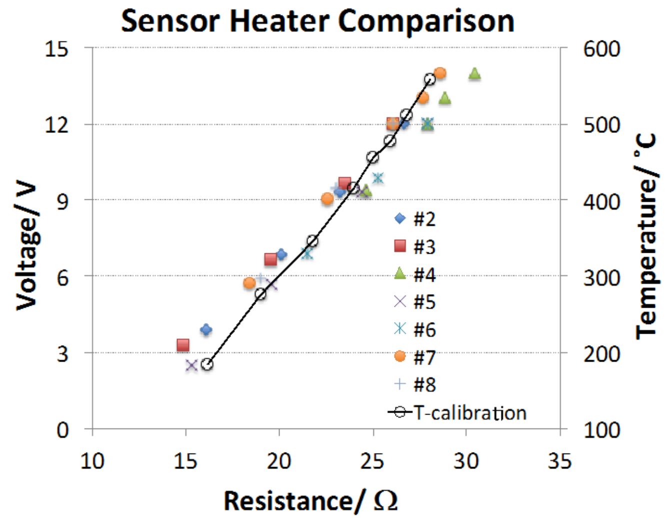
2nd generation ESL sensor: characteristics

ESL can prepare multiple devices as needed.

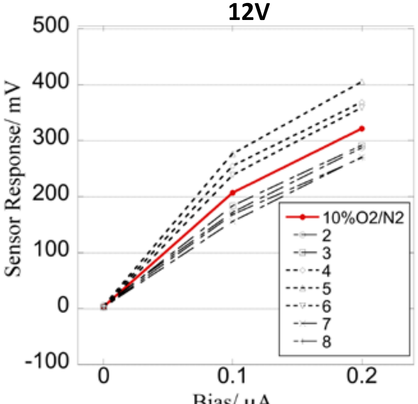


Sensor reproducibility - heater

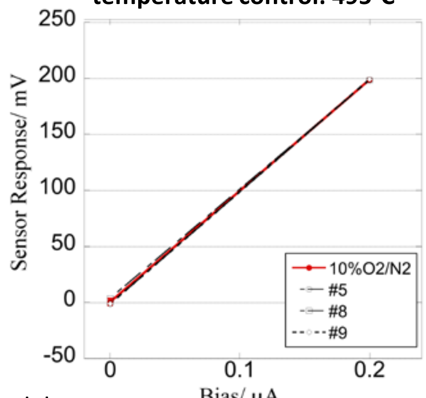


Response reproducibility 1st batch, 2nd gen

Constant heater voltage operation: 12V



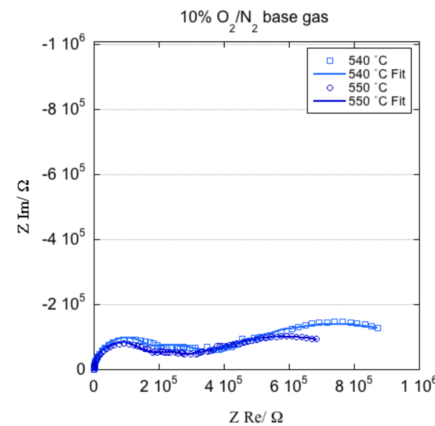
Heater resistance-based temperature control: 495˚C



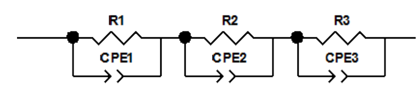
After good device reproducibility obtained, heater control circuitry designed for precise sensor temperature control.

Custom Sensor Solutions, Inc.

Sensor impedance dominated by interfacial resistance as desired



	540 ˚C	550 ˚C
R1	1.41E+05	1.21E+05
CPE1-T	4.87E-11	5.19E-11
CPE1-P	1.05	1.04
R2	1.70E+05	1.42E+05
CPE2-T	1.43E-08	4.14E-08
CPE2-P	0.73	0.62
R3	8.67E+05	6.55E+05
CPE3-T	1.53E-06	1.93E-06
CPE3-P	0.39	0.38



Replicates LANL bulk devices!

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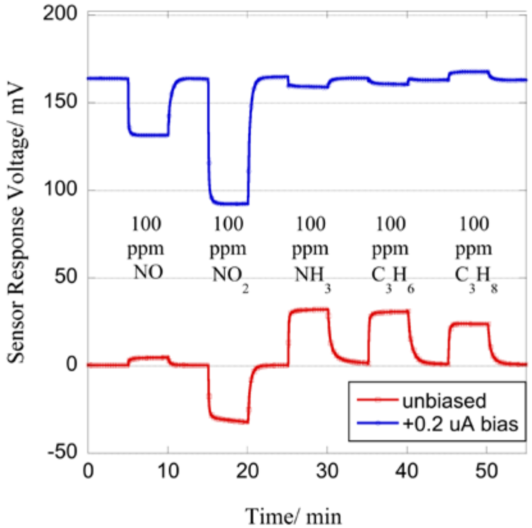
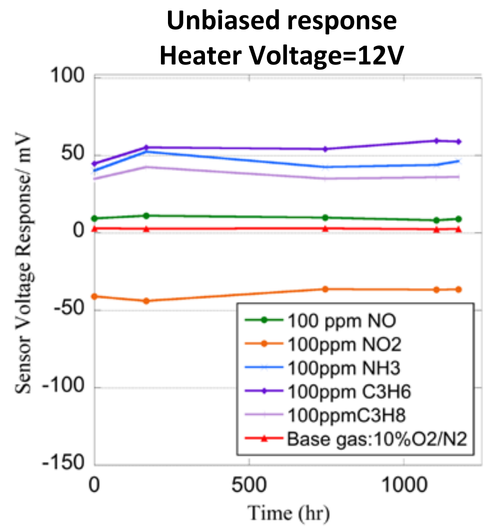
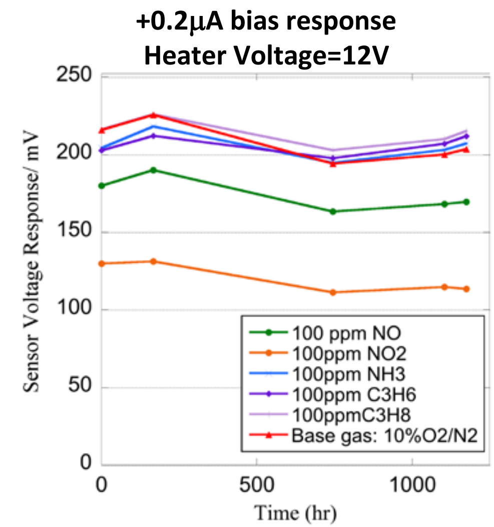
2nd generation ESL sensor: characteristics

Sensor response to application of current bias



Stability over 1000hr of testing





Effect of bias current application on NO response: